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A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

SECOND PAPER. — THE ANALYSIS OF STRONTIC CHLORIDE.

By Theodore William Richards.

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About ten years ago the first paper from this laboratory upon the subject of the atomic weight of strontium * showed that the usually accepted value 87.5 was probably about 0.2 per cent too low. This result was not a surprise, for the error had been predicted, upon the basis of a discussion of the faulty methods used by previous experimenters. The new results seemed to be trustworthy, and to represent, as well as a single series of experiments could, the true value of the constant sought.

The determination of an atomic weight by a single method is nevertheless unsatisfactory, no matter how admirable that method may be. Of course the verdict of a good method and a series of good analyses is much reinforced by an experimental proof of the flaws in other discrepant data; but the greatest of certainty is to be obtained only when the subject has been approached from several wholly different points of view. With this idea in mind, therefore, the analysis of strontic chloride was undertaken in order to confirm or disprove, as the case might be, the results of the analysis of strontic bromide described in 1894. The investigation was made in 1895–6, but has remained unpublished because of an incomprehensible discrepancy, now explained.

The balances and weights employed were those used in previous work, to which the reader is referred for all details. All weights were reduced to the vacuum standard as usual. The specific gravity of strontic chloride taken for this purpose was that given by Schroeder, 3.05, which was assumed to be correct, because his determination for baric chloride under similar conditions has often been confirmed. All the care taken in previous work at this laboratory was exercised in this case; it is unnecessary to repeat the several details.

The sample of strontic chloride used for analysis was made from a portion of the strontic carbonate remaining from the third preparation

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* These Proceedings, **30**, 369 (1894).

of strontic bromide,* and was therefore no less pure than this specimen. The carbonate had been prepared in the following manner. The so-called "pure" strontic chloride of commerce was dissolved in water, treated with ammonic hydrate and a little carbonate, and filtered from the precipitate containing iron, aluminum, and so forth. To the filtrate was added an excess of sulphuric acid, and the precipitated strontic sulphate was thoroughly washed with dilute sulphuric acid and then with pure water, in the hope of freeing it from magnesium and calcium. When the wash water became neutral to methyl orange the precipitate was treated with enough ammonic carbonate solution to convert about half of it into carbonate, and the mixed precipitate was then washed with water by decantation until only a very small constant trace of sulphuric acid (due to strontic sulphate) was found in the decantate. The carbonate was then decomposed by pure hydrochloric acid, and the solution was allowed to stand in a glass flask for nine months over the undecomposed sulphate, with occasional shaking.† Thus all but a minute trace of the barium was eliminated. The strontic chloride was decanted, the sulphate washed once with water, and the filtered decanted liquid was evaporated in a platinum dish until most of the free hydrochloric acid had been expelled. The dissolved residue was neutralized with ammonia, shaken with a little ammonic carbonate, and then filtered. To the greatly diluted filtrate was added an excess of pure ammonic carbonate, and the precipitate was washed until the wash water was free from chlorine. The strontic carbonate was dissolved in nitric acid which had been twice distilled in platinum, and the nitrate was crystallized twice successively in a platinum dish. Each quantity of crystals was washed with small quantities of water and three or four additions of alcohol. The first mother liquor, upon being fractionally precipitated by means of alcohol, showed distinct traces of calcium in the extreme solution ; thus Barthe and Falière's method was not capable of freeing the substance wholly from calcium. The second nitrate mother liquor showed no trace of calcium upon the most careful spectrometric scrutiny, although the test is one of very great sensitiveness; therefore the crystals could have contained none.‡ This effectual elimination of calcium was due no doubt to the difference in crystalline form between the calcium and strontium salts.

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* These Proceedings, **30**, 377 (1894).

† Barthe and Falières, Journ. Chem. Soc., Abs. 1892, p. 1277. Bull. Soc. Chim., [3], **7**, 104.

‡ Richards, These Proceedings, **28**, 7 (1893).

Two hundred grams of the purest crystals, after having been dried at 139°, were dissolved in about a liter of the purest water and filtered into a large platinum dish, into which was passed at first pure ammonia gas and then pure carbon dioxide through a platinum tube. The pure strontic carbonate was washed by decantation eight or ten times, dried on the steam bath, and ignited in a double platinum crucible over a Berzelius lamp. Thus were residual traces of nitrate decomposed.

The mixture of oxide and carbonate obtained in this manner was dissolved in very pure hydrochloric acid, which had been distilled in a platinum still. The chloride was evaporated to dryness, fused in a platinum dish to render silica insoluble, dissolved in purest water, allowed to stand, filtered, acidified, crystallized, and dried. That used for Analysis 1 was crystallized only once, that used for Analysis 4 was crystallized three times, while that used for Analyses 2 and 3 came from the evaporated mother liquors of the last crystallization. The essential agreement of the results from these three fractions shows that if any barium had escaped separation as sulphate, it was eliminated by the first recrystallization as chloride. This is not surprising, since baric chloride is heteromorphous with the strontic salt, these substances crystallizing with two and six molecules of water respectively, at ordinary temperatures. The previous double crystallization as nitrate could not have eliminated barium, since strontic and baric nitrates cystallize in similar anhydrous forms.

The silver used was similar to that used in the work on magnesic chloride.* It was finally prepared for weighing by fusing the electrolytic crystals in a boat of lime in a vacuum. Subsequent work has shown that this silver may have contained as much as $\frac{1}{30000}$ of its weight of oxygen, derived from the decomposition of the included argentic nitrate from which the crystals were deposited; but no correction is made for this trace of impurity, because its amount is uncertain, and because the analytical work can hardly be accurate to within one part in thirty thousand.

Before analysis the strontic chloride was fused in a current of hydrochloric acid and nitrogen, cooled in pure dry nitrogen, and transferred in its platinum boat to the stoppered weighing bottle in pure dry air. For the first determination the apparatus used with the bromide was employed for these operations, but in the last three analyses the improved form devised for the work on magnesic chloride was employed.†

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* Richards and Parker, These Proceedings, **32**, 62 (1896).

† Ibid., **32**, 58 (1896).

These last three determinations were very kindly made by Dr. H. G. Parker immediately after the completion of the magnesium work, and all the precautions discussed in that description were heeded. It is a pleasure to express my indebtedness to Dr. Parker for this assistance.

The analysis of the three fractions of crystallized salt were made by comparison with silver, using solutions at least as dilute as decinormal, and determining the end point by observing with the help of the nephelometer when the supernatant mother liquor contained equal concentrations of silver and chlorine.

A preliminary experiment with salt of less purity need not be detailed. The table below contains the essential data and results of the four consecutive final determinations, the only ones which were made.

The Ratio of Strontic Chloride to Silver.

Number of Determination.	Weight of Fused Anhydrous $SrCl_2$ (in Vacuum).	Weight of Fused Silver (in Vacuum).	Ratio 2 Ag : $SrCl_2$ = 100.000 : x.
	grams.	grams.	$x =$
1	4.2516	5.7864	73.476
2	2.4019	3.2688	73.480
3	3.5184	4.7886	73.475
4	3.0264	4.1189	73.476
			73.477

If silver is assumed to have an atomic weight of 107.93, and chlorine 35.455, according to usual custom, the atomic weight of strontium calculated from these results becomes 87.697. This result, greater by 0.033 than the value found from the bromide, indicated the presence somewhere of an unknown source of error; and the results were left unpublished for ten years because of the doubt therefore attaching to them.

This doubt has now been wholly dispelled by the discovery of an error in the assumed atomic weight of chlorine. It now appears that if silver is taken as 107.93, chlorine must be 35.473;* and the atomic weight of strontium calculated upon this basis becomes 87.661, a value essentially identical with that found from the bromide, 87.663.

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* Richards and Wells, in an investigation now being published by the Carnegie Institution. The somewhat lower value, 35.467, which was first announced as the outcome of this work, was the result of preliminary experiments only.

It must be borne in mind that the standard Ag = 107.930 is probably not precise, if oxygen is taken as 16.000. The recent work just cited has shown that the silver of Stas must have contained weighable traces of impurity, and therefore that silver must have a lower atomic weight than 107.93. Because, however, the exact value is still uncertain, the value 107.930 is still retained, in order to avoid an additional shift from one arbitrary standard to another. An alteration in the assumed value for silver affects that for strontium in direct proportion, and may therefore be applied at any time.

SUMMARY.

In this paper are detailed four determinations of the atomic weight of strontium, by comparison of strontic chloride with silver. Calculated upon the basis of the old incorrect value for chlorine, these results yield a value higher than that obtained from strontic bromide; but on the basis of the new value for chlorine 35.473 (silver being assumed as 107.930) the two different series yield almost identical results. Accordingly the new value for chlorine is confirmed by this investigation. The atomic weight of strontium is thus found as follows (Ag = 107.930).

From $SrBr_2$; Sr = *87.663*
From $SrCl_2$; Sr = *87.661*
Average Sr = *87.662*